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Note on a standard program for calculation of one-electron molecular integrals of overlap type by use of the Swedish electronic computor BESK[1]

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SUMMARY

All the combinations of overlap integrals between the hydrogen-like wave functions of $1s$, $2s$, $2p$, $3s$, $3p$ and $3d$ types can be calculated by the use of this program. This is specially constructed for overlap integrals between equal atoms, but can be used even for unequal atoms, except when the orbitals of the different atoms have equal quantum numbers. The atomic radius and the effective charges of all the orbitals must be put on the parameter tape together with the number of those integrals which will be calculated. The computation time is about 3 secs per integral if $|\beta| > 2$ or if $\beta = 0$, where β is given in (8). If $|\beta| < 2$ the time will be about 10–15 secs per integral. A special arrangement has been made in order to vary the inter-atomic distance. Partial results as the values of $A_n(\alpha)$ and $B_n(\beta)$ for $n = 0, 1, \ldots, 8$, which are defined in (3), can also be given by the program, if a special code notation will be put on the parameter tape just before the number of the integral.

The method of calculation

The wave functions Ψ are numbered by an index $K = 0, 1, \ldots, 9$ as follows:

$$\left.\begin{array}{lcccccccccc} K & 0 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\ \Psi & 1s & 2s & 2p\pi & 2p\sigma & 3s & 3p\pi & 3p\sigma & 3d\delta & 3d\pi & 3d\sigma \end{array}\right\} \tag{1}$$

The overlap integrals are numbered by two indices KL. The π- and σ-directions of the two participating atoms are chosen to be equal (parallel coordinate systems). The direction of σ goes from the first to the second atom.

All the integrals KL can be written as a linear combination of expressions of the following type:

$$\int_0^\infty \int_{-1}^{1} \prod_{\varkappa=1}^{5} (\xi^{\varepsilon_{\varkappa 1}} \eta^{\varepsilon_{\varkappa 2}} + \varepsilon_{\varkappa 3} \xi^{\varepsilon_{\varkappa 4}} \eta^{\varepsilon_{\varkappa 5}}) e^{-\alpha\xi} e^{-\beta\eta} \, d\xi \, d\eta = \sum_{\lambda=1}^{32} C_\lambda A_{\nu_\lambda}(\alpha) B_{\mu_\lambda}(\beta). \tag{2}$$

The integers C_λ, ν_λ and μ_λ of a single integral are calculated by BESK from the $\varepsilon_{\varkappa\varrho}$'s at less than 10^{-2} secs. All the $\varepsilon_{\varkappa\varrho}^{KL}$'s are placed on the program tape and will be brought over to the magnetic drum of BESK before the calculations start. The actual set of ε has been chosen by BESK according to the number KL of the integral on the parameter tape.

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[1] A new program giving all types of molecular one-electron two-center integrals of the K, L and M shells will be finished in a short time.

The calculations of the functions

$$\left.\begin{aligned} A_\nu(\alpha) &= \int_0^\infty \xi^\nu e^{-\alpha\xi}\, d\xi, \\ B_\mu(\beta) &= \int_{-1}^{1} \eta^\mu e^{-\beta\eta}\, d\eta \end{aligned}\right\} \tag{3}$$

can be made according to the well-known formulae ($\alpha \neq 0$).

$$A_\nu(\alpha) = \frac{1}{\alpha}\left[\nu A_{\nu-1}(\alpha) + e^{-\alpha}\right] \qquad A_0(\alpha) = \frac{e^{-\alpha}}{\alpha}, \tag{4}$$

$$B_\mu(\beta) = -A_\mu(\beta) - (-1)^\mu A_\mu(-\beta) \qquad (\beta \neq 0), \tag{5}$$

$$B_\mu(0) = \frac{1+(-1)^\mu}{\mu+1}. \tag{6}$$

These functions will be computed by BESK for $\mu, \nu = 0, 1, \ldots 8$ within a fraction of a second. However, the possible accuracy of the exponential functions at present at BESK, which corresponds to 12 decimals, will not at all be sufficient for calculation of the B-functions according to (5), especially for large μ-values and small β-values. It might happen that even the order of magnitude will be incorrect. To correct this, it is possible to use the following expansion of B in series, where cancelling terms in the ordinary Taylor series are omitted:

$$B_\mu(\beta) = B_\mu(0) + \sum_{\nu=1}^{\infty} \left\{\left[(-1)^\mu + (-1)^\nu\right] \frac{\beta^\nu}{\nu!} \sum_{\lambda=0}^{\mu} (-1)^\lambda \frac{\mu!\,\nu!}{(\mu-\lambda)!\,(\nu+\lambda+1)!}\right\}. \tag{7}$$

Working with (7) it might, however, take 30 secs or more for BESK to calculate an integral value. Another inconvenience is the slow convergence for large values of β, which means many additions and low accuracy. In the present program (7) will be used when $|\beta| < 2$ and (5) when $|\beta| \geq 2$. This combination always gives 8 correct decimals.

Before the calculations of the separate integrals, the values of the parameters α and β and the normalizing factors N will be calculated for all possible combinations KL according to

$$\left.\begin{aligned} \alpha_{KL} &= R\left(\frac{Z_K}{n_K} + \frac{Z_L}{n_L}\right), \\ \beta_{KL} &= R\left(\frac{Z_K}{n_K} - \frac{Z_L}{n_L}\right), \\ N_{KL} &= C_{KL}\,(RZ_K)^{n_K+\frac{1}{2}}\,(RZ_L)^{n_L+\frac{1}{2}}, \end{aligned}\right\} \tag{8}$$

where *half* the inter-atomic distance R and the effective charges Z must have been put on the parameter tape. The principal quantum numbers n and the constants C

are chosen according to the KL-number on the parameter tape. This number will also make it possible for BESK to choose the actual linear combination of (2).

The resulting value will be type-written or punched on a tape, which takes about one second. If the new rapid punch is in order, this time will be almost entirely saved. The total time per integral, printing included, will thus be about 3 secs if $|\beta| \geq 2$ (or if $\beta = 0$) and up to about 15 secs if $|\beta| < 2$. The rapid punch saves 1 sec per integral.

The program will be kept available at BESK and can be used by everybody. The price depends on the time used on BESK and will at present be 6 Sw. kronor a minute. Except for the calculating time, there will be about 2 minutes to get the program into the machine. Details concerning the managing of the program can be sent to those interested.

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